

Title	Molecular Orbital Calculations of Continuum Wavefunctions for H with Basis Functions of Atoms
Author(s)	Nakamatsu, Hirohide; Adachi, Hirohiko; Mukoyama, Takeshi
Citation	Bulletin of the Institute for Chemical Research, Kyoto University (1994), 72(1): 45-50
Issue Date	1994-03-31
URL	http://hdl.handle.net/2433/77550
Right	
Type	Departmental Bulletin Paper
Textversion	publisher

Molecular Orbital Calculations of Continuum Wavefunctions for H_2^+ with Basis Functions of Atoms

Hirohide NAKAMATSU*, Hirohiko ADACHI** and Takeshi MUKOYAMA***

Received February 10, 1994

Molecular continuum wavefunctions for H_2^+ ion are obtained by means of numerical calculations with linear combination of atomic wavefunctions. The present approach is based on the molecular orbital method which is established for the bound states of molecules. The obtained wavefunctions are compared with exact solutions which is the continuum wavefunctions of the two-center one-electron system with the Coulomb interaction. In a short range from the nuclei, the wavefunctions by the present method is in good agreement with the exact solutions. The photoabsorption cross sections are compared with the exact value reported previously.

KEY WORDS: Continuum wavefunction / Molecular orbital method / H_2^+ / Photoabsorption cross section

I. INTRODUCTION

Continuum wavefunctions for molecules are required for studies of electron excitation spectroscopies such as the photoelectron spectroscopy, the photoabsorption spectroscopy and the electron energy loss spectroscopy and for analysis of electron transfer in the atomic collision processes.

There are some calculation methods which provide the molecular continuum wavefunctions: the multiple-scattering method, various methods of the partial-wave expansion, the pseudo-bound state L^2 method and the direct numerical method. A comprehensive list of the methods which have been applied to H_2 photoionization can be found in Ref. 1. Richards et al.^{1,2)} have reported a direct numerical method where the differential equations for the continuum are solved with the finite difference method and the obtained wavefunction is joined to an asymptotic solution which stands at large distances. They have presented the photoionization cross sections with high accuracy for H_2 and H_2^+ . Their method is suitable for diatomic or linear molecules, because the system is reduced to a two-dimensional problem. At this stage, it is inconvenient for calculation of polyatomic molecules with the lower symmetry, requiring huge computation time for the three-dimensional cases. The multiple scattering method³⁾ is frequently utilized for theoretical X-ray absorption spectra. This method in the generally used form is restricted to the potential with the crude muffin-tin type. The complete

* 中松博英: Division of States and Structures, Institute for Chemical Research, Kyoto University, Uji, Kyoto 611.

** 足立裕彦: Department of Metallurgy, Faculty of Engineering, Kyoto University, Kyoto 606-01.

*** 向山 毅: Division of States and Structures, Institute for Chemical Research, Kyoto University, Uji, Kyoto 611.

expression of the continuum wavefunction is not required in the L^2 method.⁴⁻⁶⁾ Instead, continuum information is extracted from operators discretized in finite sets of square integrable (L^2) basis functions.

In the present work based on the L^2 method adopting a numerical basis set, we use a computer code named 'SCAT'⁷⁾ which puts the discrete-variational (DV) $X\alpha$ molecular orbital (MO) method into practice. We have applied this MO method to theoretical X-ray absorption spectra of molecules.⁸⁻¹⁰⁾ For the one-electron system of H_2^+ , the $X\alpha$ approximation is unnecessary. The DV integration scheme and orthogonalization procedure are used to generate the continuum wavefunctions. The standard SCAT code has been modified for including atomic continuum wavefunctions in the basis set in addition to bound-state ones.

II. COMPUTATIONAL METHOD

In the DV method, one-electron Hamiltonian matrix elements H_{ij} and overlap ones S_{ij} in the secular equation are evaluated with the weighted sum of integrand values at randomly selected sample points:

$$(\mathbf{H} - \epsilon \mathbf{S}) \mathbf{c} = 0, \quad (1)$$

$$H_{ij} = \sum_k \omega(\mathbf{r}_k) \phi_i(\mathbf{r}_k) H(\mathbf{r}_k) \phi_j(\mathbf{r}_k), \quad (2)$$

$$S_{ij} = \sum_k \omega(\mathbf{r}_k) \phi_i(\mathbf{r}_k) \phi_j(\mathbf{r}_k), \quad (3)$$

where $\omega(\mathbf{r}_k)$ is the reciprocal of the sample point density at \mathbf{r}_k . This procedure makes it easy to adopt numerical atomic orbitals as a basis set for the molecular orbitals. The atomic orbitals (AO) are used as the L^2 basis functions. Linear combination of the bound and continuum atomic wavefunctions or orbitals (LCAO) is used to approximate the continua. The wavefunctions in the spherical potential are separated into the spherical harmonics and the radial wavefunctions.¹¹⁾ The spherical harmonics are expressed with the associated Legendre functions. The differential equation for the radial wavefunction R at a position r is

$$\frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \left[-l(l+1) + r^2(\epsilon - V) \right] R = 0, \quad (4)$$

where l , ϵ and V are the angular momentum quantum number, the energy of electron and the Coulomb potential for H_2^+ . Equation (4) was numerically solved with the Hamming method. The numerical solutions for the bound states were derived with the standard computer code similar to a nonrelativistic version of the code of Liberman et al.¹²⁾ For the continuum states, the numerical outward integration was done from the origin to a finite distance. In the present work, the integration of Eq. (4) was performed up till $r = 40$ au and a quickly decreasing function of third order polynomial was joined to it with a smooth connection.

The basis functions were transformed to the symmetry-adapted orbitals for $D_{\infty h}$. When the extended basis set is used, there is the possibility that there exist almost linearly dependent basis functions. The basis functions are located on the different atoms of the molecule

but have a close relation with orbitals of the other atom because many basis functions spread out beyond the adjacent atoms. The linear dependence among the symmetry orbitals was removed before the wavefunction orthogonalization which was done by solving the secular equation.

The used basis set for the H_2^+ molecular ion consisted of orbitals from 1s to 6f and the atomic continua from 0 Hr to +1.6 Hr with an energy sequence of the equal ratio of $\sqrt{2}$ beginning at +0.05 Hr, containing s, p, d and f wavefunctions. After the removal of the linear dependence, 366 MO's were generated and 255 MO's were located above the vacuum level.

The oscillator strength f_{ij} for a transition from a state i to j was calculated in the dipole approximation:

$$f_{ij} = \frac{2}{3} \omega \left| \langle f | \mathbf{r} | i \rangle \right|^2, \quad (5)$$

where ω is the energy difference between the state i and f . Numerical integration in the dipole matrix elements was performed in the same way as that in Ref. 13. It was the same DV integration method as used in 'SCAT'. The cross section is given by

$$\sigma_{ij} = \frac{2\pi^2 \alpha a_0^2}{g_i} f_{ij} \delta(\omega - \omega_p), \quad (6)$$

where α is the fine-structure constant, a_0 is the Bohr radius, g_i is the degeneracy of the initial state and ω_p is the photon energy. For the bound states, the function δ expresses a lineshape including the exciting X-ray linewidth, the hole-state lifetime contribution and the spectrometer response. For the continuum, δ can be replaced with unity.

For comparison, exact continuum wavefunctions for H_2^+ were calculated using the computer code by Rankin and Thorson.¹⁴⁾ This calculation for the two-center one-electron system with the Coulomb interaction is based on the algorithm presented by Ponomarev and Somov.¹⁵⁾

The results for H_2^+ can be applied to any other bare-nucleus one-electron system with charge Z for each nucleus, when the distances are scaled as $1/Z$ and the energies as Z^2 .

III. RESULTS AND DISCUSSION

The continuum wavefunctions for the H_2^+ ion which were derived by the molecular orbital method in the LCAO approximation are compared with the exact solutions for the two-center one-electron system, as shown in Figs. 1 and 2. The bond length was set to 2.0 au, according to the minimum of the calculated energy.¹⁶⁾ The amplitudes of wavefunctions are normalized to one at the center of hydrogen atoms. The results by the present method are in good agreement with the exact wavefunctions. In the short range from the nuclei, the agreement is excellent.

The deviation from the exact solution is obvious in the region from 2.5 au to 10 au. In the present MO calculations, the basis functions are located at each hydrogen atom. The wavefunctions on the neighboring atom are quite different in amplitude and curvature from those on the opposite side. Through the process of the orthogonalization of the present method, the continuum wavefunctions are fitted with the basis set, using the variational method. This fit-

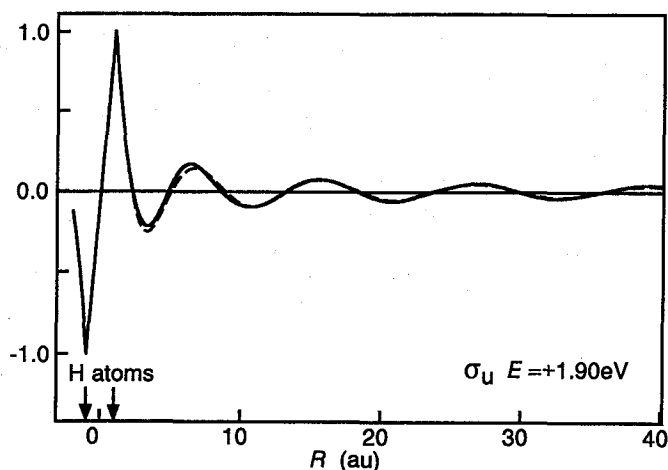


Fig. 1. Continuum wavefunctions of σ_u for H_2^+ with 1.90 eV above the vacuum level. The solid curve is calculated by the molecular orbital method and the broken curve is the exact solution. The positions of hydrogen nuclei are indicated with arrows.

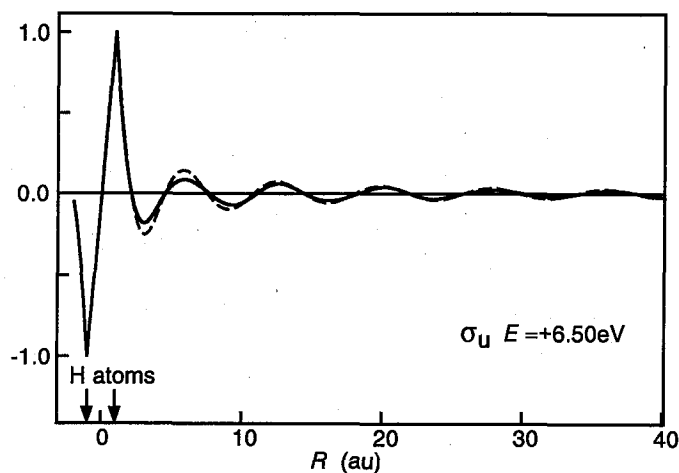


Fig. 2. Continuum wavefunctions of σ_u for H_2^+ with 6.50 eV above the vacuum level. The solid curve is calculated by the molecular orbital method and the broken curve is the exact solution. The positions of hydrogen nuclei are indicated with arrows.

ting is done more strictly in the region where the deviation in the wavefunction causes larger energetic instability, that is, in the region with the higher kinetic energy of electron. Therefore, the deviation from the exact value is large on the opposite side of the adjacent hydrogen atom.

At the greater distances, the MO continuum wavefunctions agree well again with the exact wavefunctions. Phase of the wavefunction is determined at a distant point. Phase shift of the wavefunction is valuable for estimating angular distribution of the photoelectron, which provides precise information of the orbital properties. In the direct numerical method,^{14,15)} the differential equation of the continuum is solved outward from the centers of atoms and the

obtained wavefunctions are joined to asymptotic solutions at the greater distance. The precision on applying the asymptotic solution at a short distance was estimated, using the computer code of Rankin and Thorson.¹⁴⁾ The precision of two digits for the asymptotic solution of σ_u with 1.90 eV and 6.50 eV is achieved at 23 au and 6.7 au of distances and that of four digits at 30 au and 10 au, respectively. The phase deviations of the MO continuum wavefunctions from the exact ones for σ_u with 1.90 eV and 6.50 eV are 0.04π and 0.05π , respectively, at the distance greater than 20 au. The connection at 30 au with the asymptotic solution does not deteriorate the total precision of the phase determination. Within this precision, the phase shift values can be derived from the asymptotic solutions connected with the present MO continua. To obtain the phase shift information for general molecules, wavefunctions solved at a middle distance for arbitrary spherical potentials of molecules are required. Using this solution, the wavefunction determined at a short distance from the molecule is connected with an asymptotic wavefunction at a long distance. The calculation methods for the arbitrary spherical potentials have been presented in Ref. 17.

For the photoabsorption spectra, information of the wavefunction at the long distance is not required. Since the bound electron which is to be excited by the photon occupies a small volume inside the molecule, only the continuum wavefunctions within this small volume is necessary to estimate the photoabsorption cross sections.

In the present work, the oscillator strength was converted to the photoabsorption cross section with the function δ of the Lorentzian curve. The same δ was used for the oscillator strength of the discretized continua. This procedure is based on a relation for finite intervals:

$$\sum_i^n s_i \rightarrow \int \sigma dE, \quad \text{when } n \rightarrow \infty \quad (7)$$

where s_i is the i th discretized cross section. To get a smooth photoabsorption spectrum, the peak width of each Lorentzian curve was assumed to be 2.0 eV. For the bound levels, the width is determined by the resolution of spectrometer and the natural line width. The present width for the bound levels was tentatively fixed to 2.0 eV. The theoretical photoabsorption spectrum of excitation from the state $(1s\sigma_g)^1$ is shown in Fig. 3.

A number of Rydberg states exist below the ionization energy (0 eV in Fig. 2) and form a continuous spectrum spreading up to the continuum. Above the ionization energy, the cross section decreases with the energy. The marks + are the exact values reported by Richards and Larkins.²⁾ The present cross section was calculated with the continuum wavefunctions in the LCAO approximation. The exact cross section and the present one are 0.931 Mb and 0.90 Mb, respectively, at 0 eV and 0.537 Mb and 0.47 Mb, respectively, at 5.44 eV. The cross sections by the present method agree well with the exact values but are smaller by 5-15% in the range up to 6.5 eV.

The fluctuation of the cross section becomes large at the energy above 6 eV. At the higher energy, the basis functions are less sufficient in number to represent the continua. Less fitted continuum wavefunctions are less stabilized in energy. If greater basis set is adopted, the components located at the higher energies may be redistributed to the lower energy region and may increase the cross sections to a small extent in the lower region. Langhoff et al.⁴⁾ have developed a method where the accurate cross sections are extracted with the Stieltjes imaging method from the L^2 discretized cross sections.

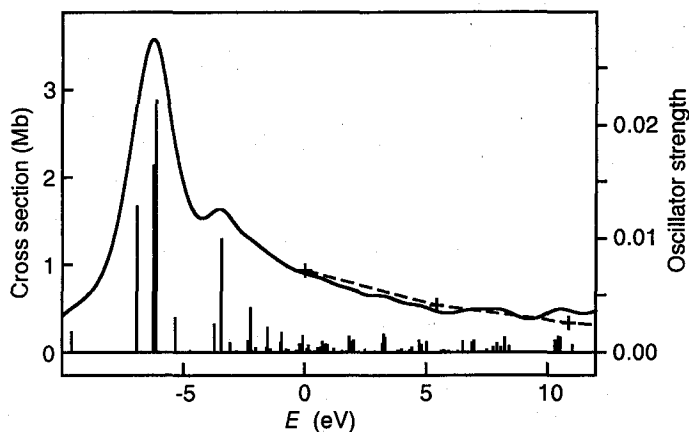


Fig. 3. Photoabsorption spectrum of excitation from $(1s \sigma_g)^1$ of H_2^+ . The abscissa indicates the excitation energy and the ionization threshold energy is set to zero. The vertical lines are oscillator strengths for the discrete levels obtained by the molecular orbital method and converted to the photoabsorption cross sections drawn with the rigid curve. The marks + are the exact values calculated by Richards et al.²⁾ and joined with the broken line.

ACKNOWLEDGMENT

The authors would like to express their grateful acknowledgment to Prof. W. R. Thorson for providing us his code for computation of the continuum states of two-center one-electron system.

REFERENCES

- (1) J. A. Richards and F. P. Larkins, *J. Phys.*, **B17**, 1015 (1984).
- (2) J. A. Richards and F. P. Larkins, *J. Phys.*, **B19**, 1945 (1986).
- (3) D. Dill and J. L. Dehmer, *J. Chem. Phys.*, **61**, 692 (1974).
- (4) P. W. Langhoff, N. Padiyal, G. Csanak, T. N. Rescigno and B. V. McKoy, *Int. J. Quantum Chem. Symp.*, **14**, 285 (1980).
- (5) W. P. Reinhardt, *Comp. Phys. Commun.*, **17**, 1 (1979).
- (6) I. Cacelli, V. Carravetta, A. Rizzo and R. Moccia, *Phys. Reports*, **205**, 283 (1991).
- (7) H. Adachi, M. Tsukada and C. Satoko, *J. Phys. Soc. Jpn.*, **45**, 875 (1978).
- (8) H. Nakamatsu, T. Mukoyama and H. Adachi, *Chem. Phys.*, **143**, 221 (1990).
- (9) H. Nakamatsu, T. Mukoyama and H. Adachi, *J. Comp. Phys.*, **95**, 3167 (1991).
- (10) H. Nakamatsu, T. Mukoyama and H. Adachi, *Jpn. J. Appl. Phys.*, **32**, suppl. 32-2, 23 (1993).
- (11) L. Pauling and E. B. Wilson, "Introduction to Quantum Mechanics", McGraw-Hill, London, (1935).
- (12) D. A. Liberman, D. T. Cromer and J. T. Waber, *Comp. Phys. Commun.*, **2**, 107 (1971).
- (13) H. Adachi and K. Taniguchi, *J. Phys. Soc. Jpn.*, **49**, 1944 (1980).
- (14) J. Rankin and W. R. Thorson, *J. Comp. Phys.*, **32**, 437 (1979).
- (15) L. I. Ponomarev and L. N. Somov, *J. Comp. Phys.*, **20**, 183 (1976).
- (16) H. Wind, *J. Chem. Phys.*, **42**, 2371 (1965).
- (17) B. Griesies and D. Dunn, *Comp. Phys. Commun.*, **77**, 313 (1993).